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MEMORANDUM

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DATE: July 20, 1999

SUBJECT: PRELIMINARY RESULTS OF ACUTE AND CHRONIC TOXICITY TESTING OF SURFACE WATER MONITORED IN THE SAN JOAQUIN RIVER WATERSHED, WINTER 1998-99

SCOPE OF THIS MEMORANDUM:

This memorandum provides results of water sampling conducted on the San Joaquin River (SJR) by the Department of Pesticide Regulation (DPR) for the Dormant Spray Water Quality Program. Information presented is from December 7, 1998 to March 5, 1999 and includes results from chemical analyses conducted by the California Department of Food and Agriculture (CDFA) and bioassays conducted by the California Department of Fish and Game (DFG). This memorandum summarizes one-year of a five-year study begun in 1996, designed to monitor dormant spray insecticides (chlorpyrifos, diazinon, and methidathion) in the SJR watershed. In an effort to obtain more information about pesticide residues in surface water, samples were analyzed for additional insecticides as well as selected herbicides. This memorandum does not include an in-depth interpretation of the data which will be provided in the final report.

BACKGROUND:

The SJR flows west from the Sierra Nevada Mountain Range, then flow heads north through the San Joaquin Valley and terminates in the Sacramento-San Joaquin Delta. The river extends approximately 134 miles from Friant Dam to Stevinson where flows are intermittent, and from Stevinson to Vernalis (about 60 miles) where flows are perennial (Figure 1). The river basin including tributary watersheds, drains approximately 15,880 square miles (Central Valley Regional Water Quality Control Board, 1994). Runoff from rainfall occurring in the San Joaquin Valley and Sierra Nevada foothills during the rainy season, October to March, creates short term increases in river discharge. With little significant rain from June to September, river discharge during the summer is composed of dam releases of snow-melt water which is subsequently used

for agricultural, urban, recreational and wildlife purposes. The dormant spray season for nut and stone fruit trees coincides with the rainy season. During this period dormant spray insecticides, mainly chlorpyrifos, diazinon and methidathion, are applied along with weed oil to control peach twig borer, San Jose scale, European red mite and brown mite pests. Rainfall and subsequent surface runoff from agricultural areas provides a mechanism for off-site movement of pesticides to the SJR. From 1988 to 1990, the Central Valley Regional Water Quality Control Board (CVRWQCB) conducted an aquatic toxicity survey in the San Joaquin Valley. Surface water samples collected from certain reaches of the San Joaquin River watershed during this survey were acutely toxic to the water flea, *Ceriodaphnia dubia* (Foe and Connor, 1991). The cause of toxicity was not determined but was attributed to pesticides in general. Further study was conducted in the Valley during the winter of 1991-92, and the resultant toxicity was attributed to the presence of chlorpyrifos and diazinon (Foe and Sheipline, 1993; Foe, 1995; Kuivila and Foe, 1995). The toxicity found in these studies was in violation of the CVRWQCB's narrative water quality objective (Foe, 1995) which states that, "All waters shall be maintained free of toxic substances in concentrations that produce detrimental physiological responses in human, plant, animal, or aquatic life"
(CVRWQCB, 1994).

DPR monitored the SJR watershed during the winters of 1991-92 and 1992-93, and reported the detection of chlorpyrifos, diazinon, and methidathion in 10, 72, and 18 percent of the 108 water samples collected, respectively. Of these positive samples, 2, 13, and 1 percent respectively, exceeded the LC_{50} for *C. dubia* indicating potential acute toxicity to this organism (Ross, *et al.*, 1997). In addition, in a 1993 CVRWQCB study, diazinon concentrations in the San Joaquin River at Vernalis ranged from 0.148 to 1.07 μg/L on 12 consecutive days, and the authors concluded that chronic toxicity due to diazinon might be problematic at this site (Kuivila and Foe, 1995). Diazinon was also detected at levels acutely toxic to *C. dubia* in Orestimba Creek, a tributary to the SJR, during the 1992-93 dormant spray period (Domagalski, 1995). Consequently, methods designed to reduce the mass of dormant spray insecticides leaving target areas have been under investigation by DPR and growers (Ross, *et al.*, 1997; Ando, 1996; Anonymous, 1996; Biermann, 1996).

A U.S. Geological Survey (USGS) report of an investigation of pesticides in storm runoff from agricultural areas at a site along the Tuolumne River and from urban drains in Modesto, California found six different pesticides in the predominantly agricultural samples and 15 in the mainly urban runoff samples (Kratzer, 1998). Diazinon and chlorpyrifos were the insecticides detected in agricultural runoff in 100 and 88 percent of the 8 samples, respectively. Diazinon, carbaryl, chlorpyrifos, and malathion were each detected in 100% of the 10 urban samples collected. The herbicides simazine, napropamide and dacthal were detected in 100% of the 8 samples collected from the agricultural runoff site and also metolachlor in 88% of the samples. Simazine, dacthal and trifluralin were detected in all the samples collected in the urban runoff, and metolachlor, EPTC, benfluralin, pendimethalin, prometon, napropamide, and propanil were detected in 10 to 90% of the samples.

During the winter of 1996-97, DPR conducted toxicity monitoring at two sites in the SJR Watershed (Bennett *et al.*, 1998). The first half of winter was unusually wet with flooding followed by unseasonably dry weather during the second half of winter. Water samples from Orestimba Creek contained residues of diazinon, carbofuran, and dimethoate in 20, 13, and 7 percent of the 15 samples collected, respectively. The maximum diazinon, carbofuran, and dimethoate concentrations detected were 0.092, 0.238, and 0.082 ug/L, respectively. Three (12%) of the 24 water samples from the SJR near Vernalis contained diazinon residues, with a maximum concentration of 0.070 ug/L. *Ceriodaphnia dubia* survival ranged from 40 to 100 percent for acute toxicity tests from Orestimba Creek. Only one of the samples collected on January 29, 1997 was significantly different from the control. However, there were no pesticides detected in this sample. Chronic toxicity was not detected in the eight weekly sets of water samples collected from the SJR near Vernalis.

During the study last winter, 1997-98, river discharge remained high from January through the end of sampling in March compared to historical levels for these months (Anderson *et al.*, 1995). It was a wet season (Department of Water Resources, 1998) much like the winter before. Chlorpyrifos and methyl parathion were each detected once at 0.093 and 0.190 ug/L, respectively, in the same sample collected from Orestimba Creek on January 26, 1998. Diazinon was detected in three of 18 samples (17%) collected at the site with concentrations ranging from 0.059 to 0.139 ug/L. Diazinon was detected on January 12 and then again in the samples collected on February 2 and 4. Four of the nine herbicides analyzed for were detected in Orestimba Creek. Bromacil was detected in three of the 18 samples (17%) with concentrations ranging from 0.066 to 0.115 ug/L. Cyanazine was detected in one of 18 samples (6%) at 0.25 ug/L. Diuron was detected in six of 18 samples (33%) at concentrations ranging from 0.078 to 0.388 ug/L and simazine was detected in five of 18 samples (28%) at concentrations ranging from 0.063 to 0.711 ug/L. Three of the samples collected on December 1, 1997, January 12 and 19, 1998 each contained residues of three different herbicides.

For acute toxicity tests conducted on Orestimba Creek samples, four of 18 samples had significantly reduced survival compared to the control. The four samples were collected on January 21, and February 4, 11 and 23. Pesticides analyzed in this study were all below detection limits in the January 21 and February 11 and 23 samples. The only sample with reduced survival that correlated with a detection was collected on February 4, with diazinon, diuron and simazine detections.

During the same study period, at the San Joaquin River, diazinon and methidathion were detected. Diazinon was detected in 10 of 30 samples (33%) collected at Vernalis (Table 6). These detections came in two groupings. The first detection occurred on January 7 and was at the detection limit. There was no detection January 9. On January 12, 14 and 16 diazinon was again detected at concentrations ranging from 0.063 to 0.102 ug/L. The second group of detections began on January 30 and continued through February 11 with concentrations ranging from 0.042 to 0.093 ug/L. Methidathion was detected in three samples (10%) collected on January 7, 12 and February 2. The three detections ranged from 0.053 to 0.112 ug/L and coincided with diazinon detections. The herbicides bromacil, cyanazine, diuron and simazine were also detected in the SJR. Bromacil was detected in four (13%) and cyanazine in two of 30 samples (7%). Diuron was detected in all samples at concentrations ranging from 0.056 to 2.95 ug/L. Simazine was detected in 16 samples (53%) with levels ranging from 0.050 to 0.470 ug/L.

There was no *C. dubia* survival in the chronic toxicity test sample collected on February 2 with renewal water collected February 4 and 6. The sample collected on February 2 had detectible levels of diazinon, methidathion, diuron and simazine and there were no detections in the February 4 and 6 samples. There was no significant toxicity found in the remaining samples.

This study is part of a five-year effort to monitor the occurrence of toxicity to *C. dubia* in water collected from the SJR watershed. Monitoring was conducted specifically during winter months for organophosphate and carbamate insecticides that are historically applied to dormant nut and stone fruit orchards (Table 1). Orestimba Creek, a small tributary of the SJR, was monitored for acute toxicity since small tributaries historically carry higher insecticide concentrations than the mainstem of the SJR. Orestimba Creek contains runoff from the coastal range and agricultural areas in the valley floor. The SJR at Vernalis, a site downstream from agricultural and urban areas, yet above tidal influence from the delta, was examined for chronic toxicity. Additionally, in order to gain more information about pesticide residues in state surface waters, samples were analyzed for selected herbicides (Table 1). A companion study was also conducted to monitor pesticide levels and toxicity in the Sacramento River (Nordmark, 1998). Long-term monitoring of acute and chronic toxicity will help scientists at DPR to evaluate the effectiveness of programs designed to decrease the runoff of dormant spray insecticides.

MATERIALS AND METHODS:

Site Description

The same sites were selected as in the two previous studies. One site each was selected for acute and chronic toxicity monitoring. Acute toxicity was monitored in Orestimba Creek, a western tributary to the SJR, where runoff in the winter is composed of drainage from the Coastal Range and from agricultural areas in the watershed (Figure 1). Samples for chronic toxicity were collected from the SJR near Vernalis, where discharges from the River's major agricultural tributaries, including the Merced, Tuolumne, and Stanislaus Rivers, are received. Discharge records for both monitoring sites were available from collocated gaging stations.

Sample Collection

Background samples were collected during the week of December 7, 1998, prior to the onset of the dormant spray season. Dormant-season sampling began on January 4, 1999, and continued through March 5, 1999, when dormant-spray applications ceased.

Chemical analyses were performed on each water sample that was collected for acute or chronic toxicity tests. Pesticides included in our analyses were chosen based on historical use during the dormant spray season in the watershed (DPR, 1995), previous detections in the watershed, and to standardize analyses between the Sacramento and San Joaquin River studies. For this study, organophosphate and carbamate insecticides and soil applied herbicides (triazine herbicides, diuron and bromacil) were analyzed in three separate screen analyses with diazinon being analyzed in a fourth (Table 1).

Acute toxicity tests were performed twice per week, with samples collected on Monday and Wednesday. One chronic toxicity test was conducted weekly using water samples collected on Monday, Wednesday and Friday. Water collected on Monday was used to begin the chronic toxicity tests. Water collected on Wednesday and Friday was used to renew chronic test water.

Water samples were collected at center channel at both Orestimba Creek at River Road and the SJR near Vernalis. Each sample was taken using a depth-integrated sampler (D-77), equipped with a Teflon® bottle and nozzle. When flow was too low to use the D-77 sampler at Orestimba Creek, a Teflon® bottle attached to a pole was used to collect the sample. At both sites, sub-samples were composited in a larger 38-liter stainless steel container until 12 liters were collected. This composited sample was stored on wet ice until it was delivered to the DPR West Sacramento field office later that day.

Samples were transported to the field office and split using a Geotech® 10-port splitter, into nine 1-liter amber glass bottles with Teflon® lined caps. For both sites, two 1-liter samples were submitted to DFG for toxicity testing. Four 1-liter samples were submitted for chemical analyses: one each for the organophosphate, carbamate, diazinon and herbicide analyses. Two 1-liter backups were stored at West Sacramento and one-liter was used for acidification purposes (see below).

Samples designated for organophosphate and carbamate chemical analysis were preserved by acidification with 3N hydrochloric acid to a pH of between 3.0 to 3.5. Most organophosphate and carbamate pesticides are sufficiently preserved at this pH (Ross *et al.*, 1996). Diazinon; however, rapidly degrades under acidic conditions and therefore was analyzed from a separate unacidified sample. Herbicide samples are stable enough without acidification so were not acidified. Samples were stored in a 4°C refrigerator until transported to the appropriate laboratory (on wet ice) for analysis. All primary samples were delivered to the testing laboratory the same day they were collected except when there was a Monday holiday, then samples were delivered early on Tuesdays.

<u>Environmental Measurements</u>

Temperature and dissolved oxygen (DO) were measured *in situ,* and pH and electrical conductivity (EC) were measured on site. Water temperature and DO were measured with a Yellow Springs Instruments® DO meter (model 57). Water pH was measured with a Sentron® pH meter (model 1001). EC was measured with an Orion® conductivity meter (model 140). Additionally, alkalinity, hardness, and ammonia were measured by the DFG aquatic toxicity lab upon delivery of their samples. Totals of alkalinity and hardness were measured with a Hach® titration kit. Total ammonia was measured with an Orion® multi-parameter meter (model 290A) fitted with an Orion® ammonia ion selective electrode (model 95-12).

Daily rainfall and discharge data were also gathered for the study area. Daily rainfall measurements were obtained courtesy of the Modesto Irrigation District office in Modesto, California about 15 miles east of the Vernalis site (Modesto Irrigation District, 1999) and Yancey Lumber and Hardware in Patterson, California, eight miles north west of the Orestimba Creek site (Figure 1) (Quiroba, 1999). Discharge data were collected at collocated USGS gaging stations at both the SJR at Vernalis and Orestimba Creek at River Road. Rainfall and discharge information will be used to follow annual changes in pesticide concentrations with respect to fluctuations in flow and will also be useful for modeling efforts, should they be undertaken.

Pesticide Analysis and Toxicity Tests

Pesticide analyses were performed by the CDFA Center for Analytical Chemistry. The organophosphate insecticides were analyzed using gas chromatography (GC) equipped with a flame photometric detector. The carbamate insecticides were analyzed using high performance liquid chromatography (HPLC), post column-derivatization and a fluorescence detector. The herbicides (triazine herbicides, diuron and bromacil) were analyzed by both HPLC equipped with a UV detector and by GC equipped with a nitrogen phosphorus detector. The pesticides and reporting limits are listed in Table 1. Detailed analytical methods will be provided in the final report.

Quality control (QC) for the chemistry portion of this study was conducted in accordance with Standard Operating Procedure QAQC001.00 (DPR, 1996) and consisted of a continuing QC program, plus the submission of five rinse blanks of the splitting equipment and 38 blind spikes submitted for the Sacramento and San Joaquin studies. Blind spike and continuing QC results for each of the analytical screens are presented in Tables 2 though 6. Study 178 and 179 refer to the Sacramento and San Joaquin River studies, respectively. There were no detections of any pesticides in any of the five rinse blank samples (not in tables). The 38 blind spikes were submitted for both studies along with the regular field samples. The blind spikes contained 54 chemical analytes (Table 2). More detailed quality control data, including method development, the establishment of control limits, spike recoveries and analysis of QC will be included in the final report.

Toxicity Tests

For Orestimba Creek, one sample per collection event was delivered to DFG's ATL for acute toxicity testing. Acute tests were performed in undiluted sample water using 96-hour, static-renewal bioassays with the cladoceran *C. dubia* in accordance with current U. S. Environmental Protection Agency procedures (U.S. EPA, 1993). From the SJR, one sample per collection event was delivered to DFG's ATL for chronic toxicity testing. Chronic tests were performed using a 7-day bioassay with *C. dubia* in accordance with current U.S. EPA (1994) procedures. Test organisms used in chronic testing were placed in sample water on day one of the testing, with test water replenished on days three and five with new water collected from the site on Wednesdays and Fridays. All bioassays were commenced and renewal water used within 36 hours of sample collection except for one sample that was restarted at 77 hours due to a failed control. Data were reported as the percent survival for both acute and chronic tests, and the average number of offspring per female adult (fecundity) for the chronic tests.

RESULTS:

Environmental Measurements

Orestimba Creek
Temperature measurements at the Orestimba Creek site ranged between 4.8 and 14 °C (Figure 2). Dissolved oxygen ranged from 8.5 to 12.1 mg/L (Figure 2), with percent saturation ranging from 77 to 99%. pH ranged between 7.2 and 8.0 and EC measurements ranged from 283 to 1,006 μS/cm. Alkalinity ranged from 54 to 248 mg/L and hardness was between 76 and 406 mg/L. Ammonia concentrations ranged from below the detection limit of 50 μg/L to 392 μg/L.

Compared to the two previous dormant-spray seasons, this season was much drier. During the weekly monitoring period from January 4 to March 5, 1999, rainfall reported at Patterson, California totaled 2.82 inches (Quiroba, 1999) (Figure 3). During last year's study 11.8 inches of rain was recorded at the same site. Daily mean discharge at the USGS gaging station along Orestimba Creek at River Road ranged from 3.3 to 161 cfs (cubic feet per second). These data are provisional and subject to change.

San Joaquin River near Vernalis
Water temperature measurements at the SJR site ranged from 6.0 to 13 °C (Figure 4). Dissolved oxygen ranged from 9.1 to 11 mg/L(Figure 4), with percent saturation ranging from 87 to 99%. pH ranged from 6.8 to 8.1 and EC measurements were between 178 and 668 μS/cm. Alkalinity ranged from 36 to 144 mg/L and hardness from 44 to 198 mg/L. Ammonia concentrations ranged from below the detection limit of 50 μg/L to 256 μg/L.

During the weekly monitoring period from January 4 to March 5, 1999, discharge at the SJR site ranged from 2,722 to 15,578 cfs (Figure 5). Rainfall data collected by the Modesto Irrigation District (MID) totaled 5.20 inches during the same period (MID, 1999). Last year's rainfall totaled 12.7 inches during the same three month period at the same site.

Pesticide Concentrations and Toxicity Data

Pesticide Concentrations

During this study there were no detections of organophosphate or carbamate insecticides in the 20 samples collected at the Orestimba Creek site (Table 7). However, several herbicides were detected. Diuron was detected in all 20 samples at concentrations ranging from 0.061 to 1.7 μg/L (Figure 3). Bromacil was detected three times (15%) at concentrations ranging from 0.080 to 0.089 μg/L and simazine four times ranging from 0.066 to 0.10 μg/L. Cyanazine and prometryn were each detected once (5%) at 0.37 and .076 μg/L, respectively. Five samples (25%) contained more than one herbicide residue. Five herbicides were detected in one sample that was collected one day after a rain event on February 22, 1999. There was no significant mortality detected in any acute toxicity sample collected at Orestimba Creek.

Diazinon was detected in three of the 30 samples (10%) collected from the SJR at Vernalis (Table 7). The detections occurred on January 20, 1999 at 0.15 μg/L, January 21 at 0.090 μg/L and on February 10 at 0.053 μg/L (Figure 5). Each detection occurred 1 to 2 days after a rain event. Similar to the Orestimba Creek samples, there were no other organophosphate or carbamate insecticides detected. Diuron was detected in every sample collected at Vernalis ranging in concentration from 0.10 to 1.9 μg/L (Figure 5). Bromacil was detected in one of 30 samples (3.3%) at a concentration of 0.059 μg/L. Cyanazine came in two pulses, and was detected in a total of six samples (20%) ranging in concentrations from 0.097 to 0.42 μg/L. Prometryn was detected in two samples (7%) ranging from 0.053 to 0.071 μg/L and simazine was detected seven times (23%) with concentrations ranging from 0.059 to 0.12 μg/L. Thirteen samples (43%) had more than one triazine detection and three of them (10%) had three detections in one sample. There was no significant mortality in any chronic toxicity sample collected at the SJR.

If you have any questions, please feel free to call me.

References

Anderson S.W., P.D. Hayes, and G.L. Rockwell. 1995. Water resources data California, Water year 1994. Volume 3. Report CA-94-3. U.S. Geological Survey. Sacramento, California

Ando, C. 1996. Investigation of possible management practices to reduce dormant spray runoff from soil plots (study protocol). California EPA/Department of Pesticide Regulation, Environmental Hazards Assessment Program. May 24, 1996.

Anonymous, 1996. Everett Souza shares HUA story. Westside Water, March 1996.

Bennett, K.P., Nordmark, C.E. J. Schuette, H. Feng, J. Hernandez, and P. Lee. 1998. Occurrence of aquatic toxicity and Dormant-spray pesticide detections in the San Joaquin River Watershed, winter 1996-97. Department of Pesticide Regulation. Environmental Hazards Assessment Program. Sacramento, CA. Report # EH 98-02.

Biermann, H. 1996. Study 152: Effect of ground cover on dormant spray runoff from orchards (study protocol). Department of Pesticide Regulation, Environmental Hazards Assessment Program. November 1996.

CVRWQCB, 1994. (Central Valley Regional Water Quality Control Board) Water quality control plan (Basin Plan): Central Valley Region, Sacramento River and San Joaquin River Basins. December 9, 1994.

Department of Pesticide Regulation. 1995. Pesticide Use Report Database. Sacramento, CA.

Department of Pesticide Regulation. 1996. Standard Operating Procedure for Chemistry Laboratory Quality Control. SOP # QAQC001.00. DPR, Environmental Hazards Assessment Program. Sacramento, CA.

Department of Water Resources. 1998. web site address: http//cdec.water.ca/cgi-progs/iodir/WSIHIST .

Domagalski, J.L. 1995. Nonpoint sources of pesticides in the San Joaquin River, California: input from winter storms, 1992-93. U.S. Geological Survey Open-File Report 95-165. National Water-Quality Assessment Program. Sacramento, California.

Foe, C. 1995. Insecticide concentrations and invertebrate bioassay mortality in agricultural return water from the San Joaquin Basin. Central Valley Regional Water Quality Control Board. December 1995.

Foe, C. and V. Connor. 1991. San Joaquin Watershed bioassay results, 1988-90. Central Valley Regional Water Quality Control Board. July 1991.

Foe, C. and R. Sheipline. 1993. Pesticides in surface water from applications on orchards and alfalfa during the winter and spring of 1991-92. Central Valley Regional Water Quality Control Board. February 1993.

Quiroba, P. 1999. Personal communication. Provided daily rainfall data collected at Yancey Lumber and Hardware Store in Patterson, CA. Data deemed reliable by staff at CDF, Del Puerto Station in Patterson.

Kratzer, C.R. 1998. Pesticides in storm runoff from agricultural and urban areas in the Tuolumne River Basin in the vicinity of Modesto, California. U.S. Geological Survey, Water-Resources Investigaions report 98-4017. National Water-Quality Assessment Program. Sacramento, California.

Kuivila, K. And C. Foe. 1995. Concentrations, transport and biological effects of dormant spray pesticides in the San Francisco estuary, California. Environ. Toxicol. Chem. 14(7):1141-1150.

Modesto Irrigation District, 1999. 1998-99 rainfall records. Personal communication with D. Bakker. April 8, 1999.

Nordmark, C. 1998. Study 178:Protocol for monitoring acute and chronic toxicity in the Sacramento River Watershed, Winter 1998-99. Department of Pesticide Regulation.

Ross, L.J., R. Stein, J. Hsu, J. White, and K. Hefner. 1996. Distribution and mass loading of insecticides in the San Joaquin River, California: Winter 1991-92 and 1992-93. Department of Regulation. Environmental Hazards Assessment Program. Sacramento, California. Report # EH 96-02.

Ross, L.J., K.P. Bennett, K. D. Kim, K.Hefner, J. Hernandez. 1997. Reducing dormant spray runoff from orchards. Department of Pesticide Regulation. Environmental Hazards Assessment Program. Sacramento, California. Report # EH 97-03.

U.S. Environmental Protection Agency. 1993. Methods for measuring the acute toxicity of effluents and receiving waters to freshwater and marine organisms. 4th ed. EPA/600/4-90/027F. August 1993.

U.S. Environmental Protection Agency. 1994. Short-term methods for estimating the chronic toxicity of effluents and receiving waters to freshwater organisms. 3rd ed. EPA-600-4-91-002. July 1994.

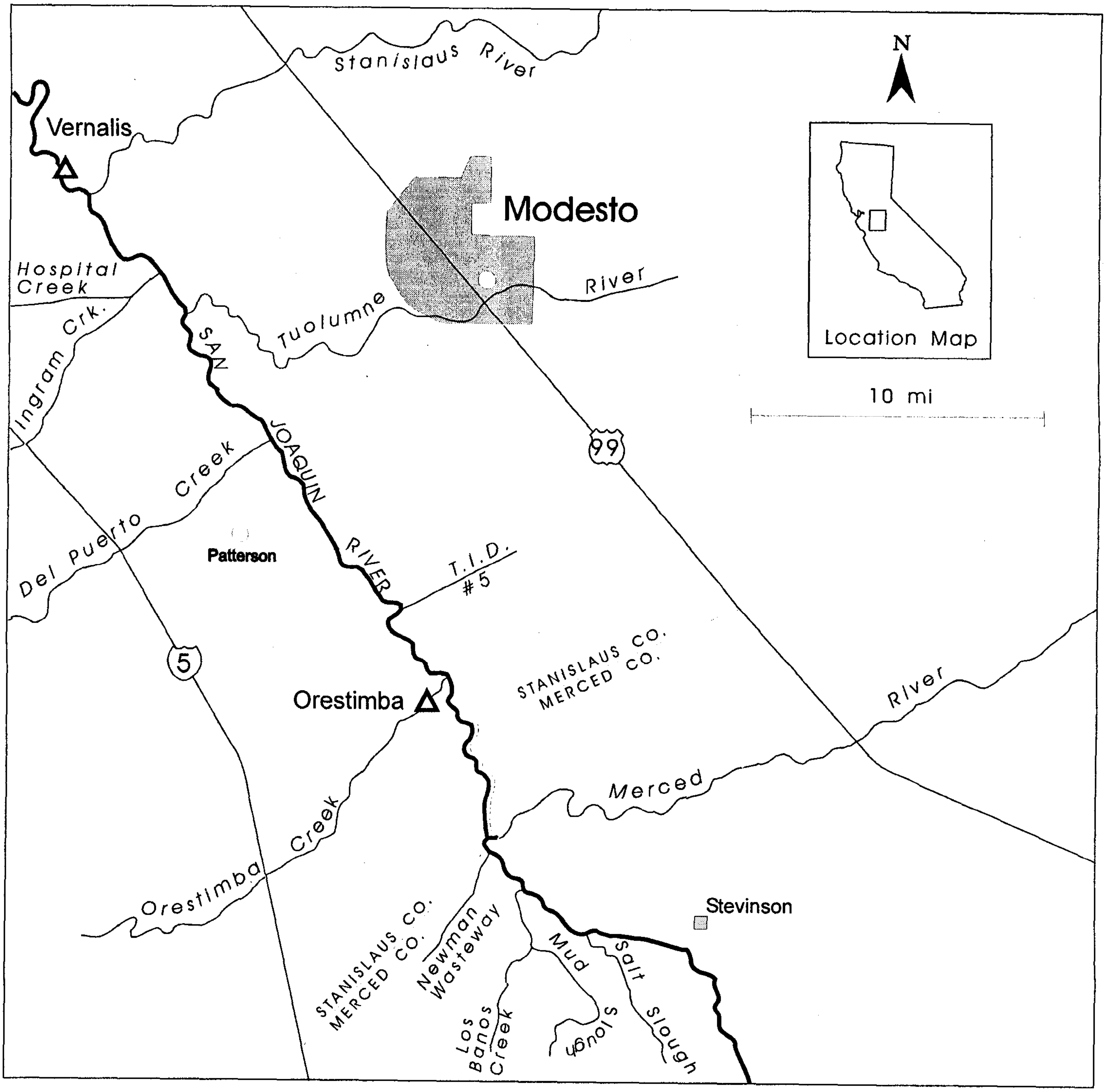

Figure 1. Location of toxicity sampling sites (**Δ**) and rainfall stations (○) in the San Joaquin River Watershed: Winter 1998-99.

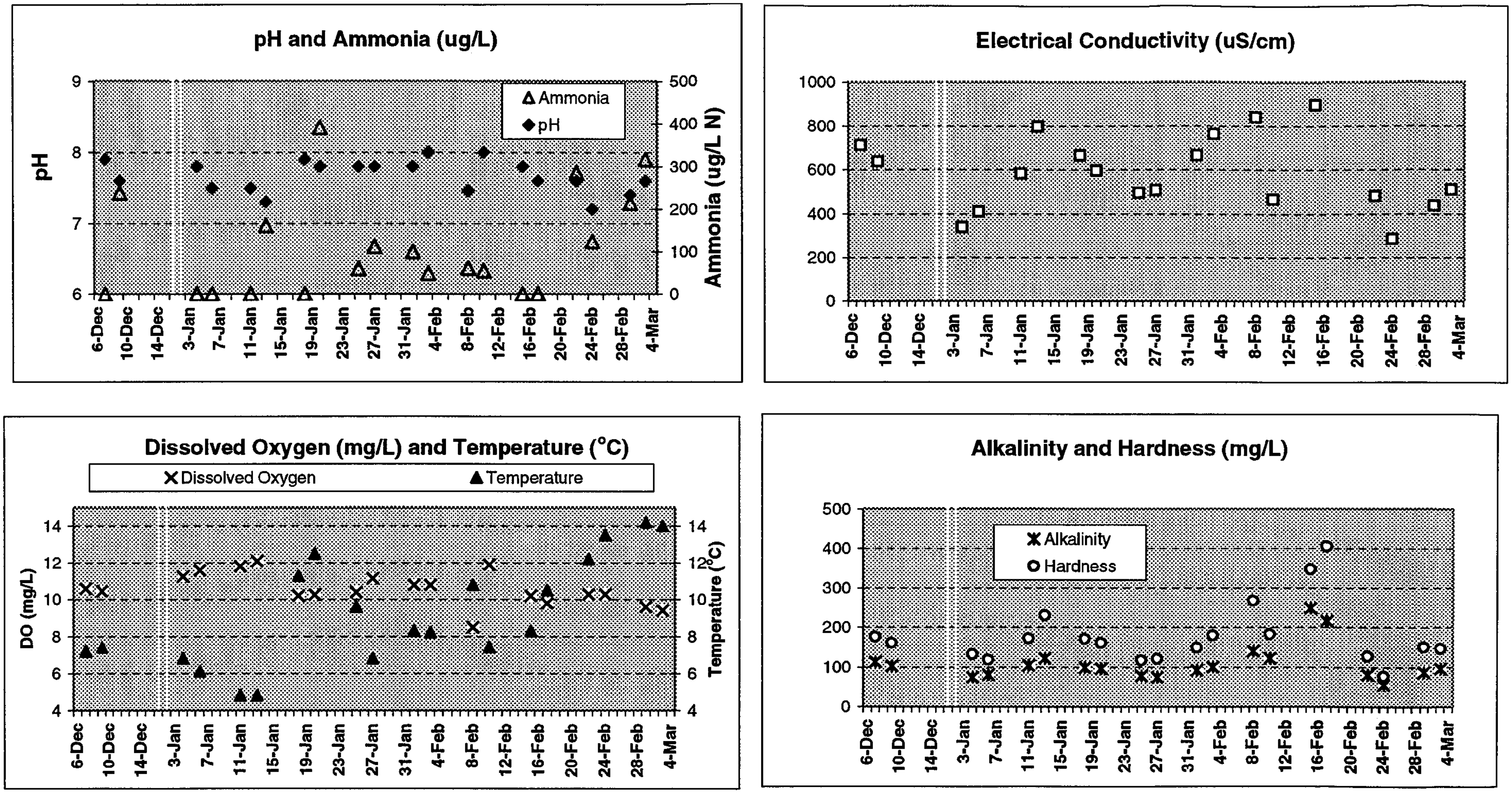

Figure 2. Environmental measurements for the Orestimba Creek at River Road. Data collected from December 7 through 9, 1998 and January 4 through March 3, 1999. Data were collected twice each week during the study period. Double bar denotes a break in sampling between background and dormant season samples.

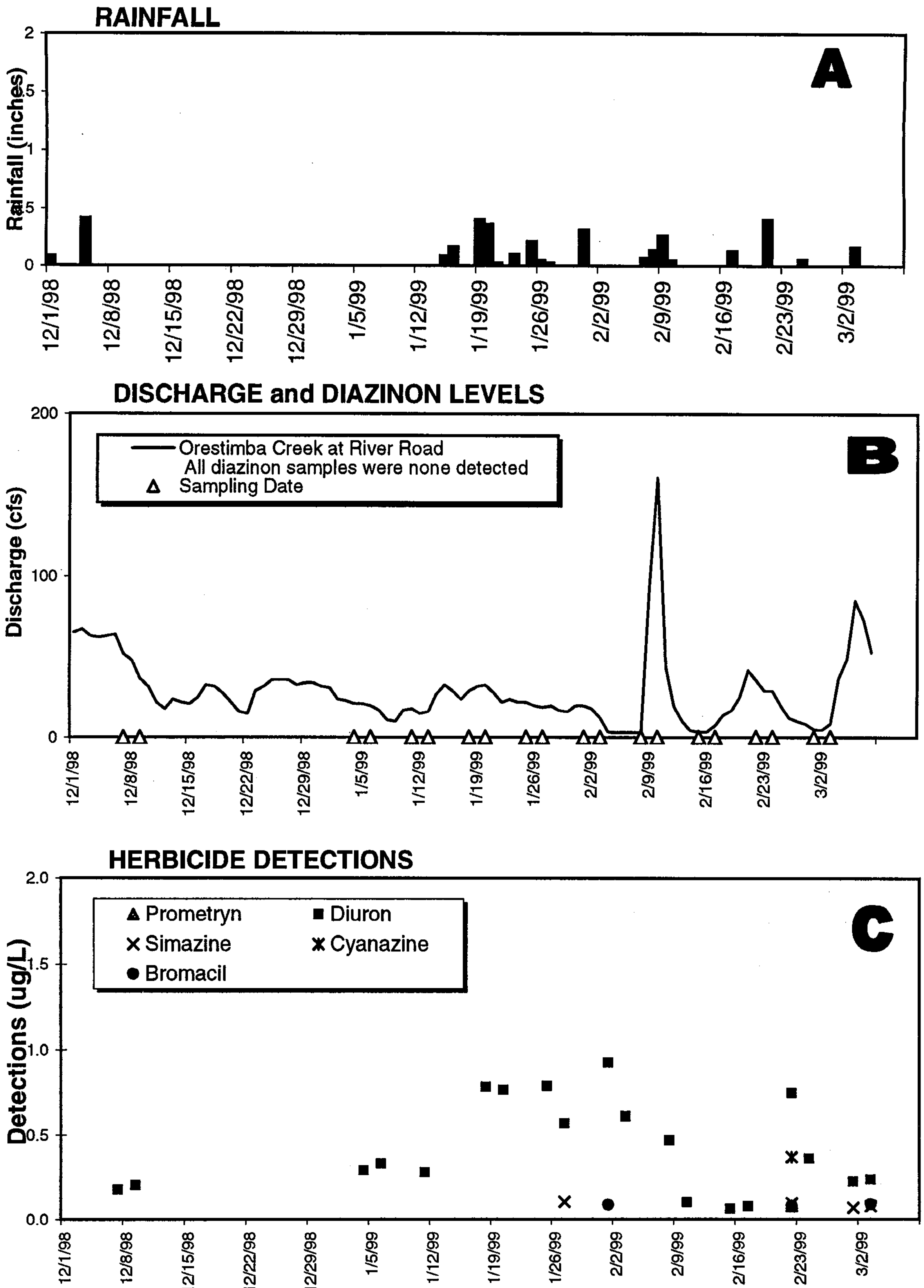

Figure 3. (A) Rainfall measured at Patterson; (B) discharge and diazinon were measured in Orestimba Creek at River Road; (C) detections of herbicides, winter 1998-99.

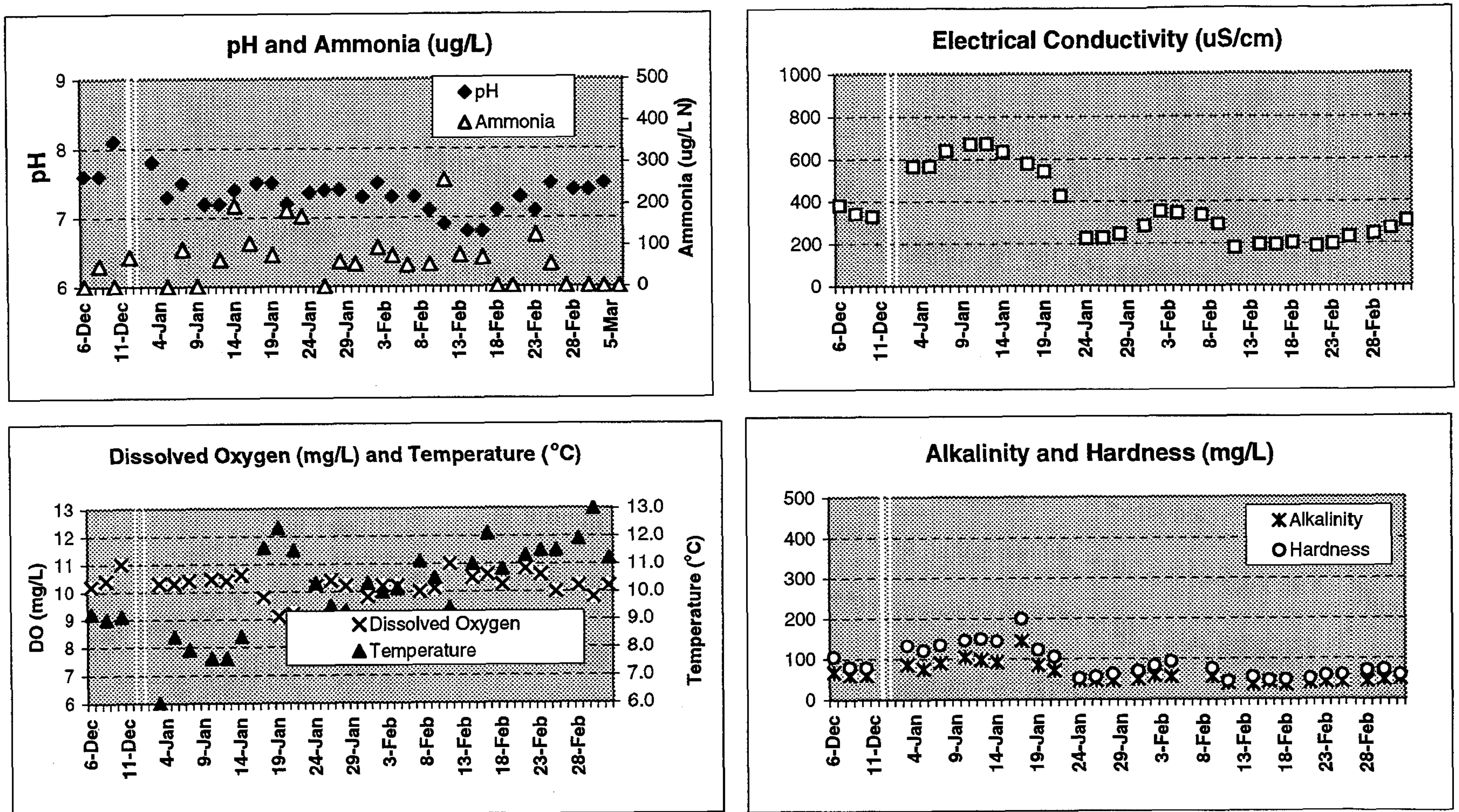

Figure 4. Envrionmental measurments for the San Joaquin River at Vernalis, CA. Data collected from December 6 -11, 1998 and January 4 through March 5, 1999. Measurements were collected three times per week during the study period. Double bar denotes a break in sampling between background and dormant season samples.

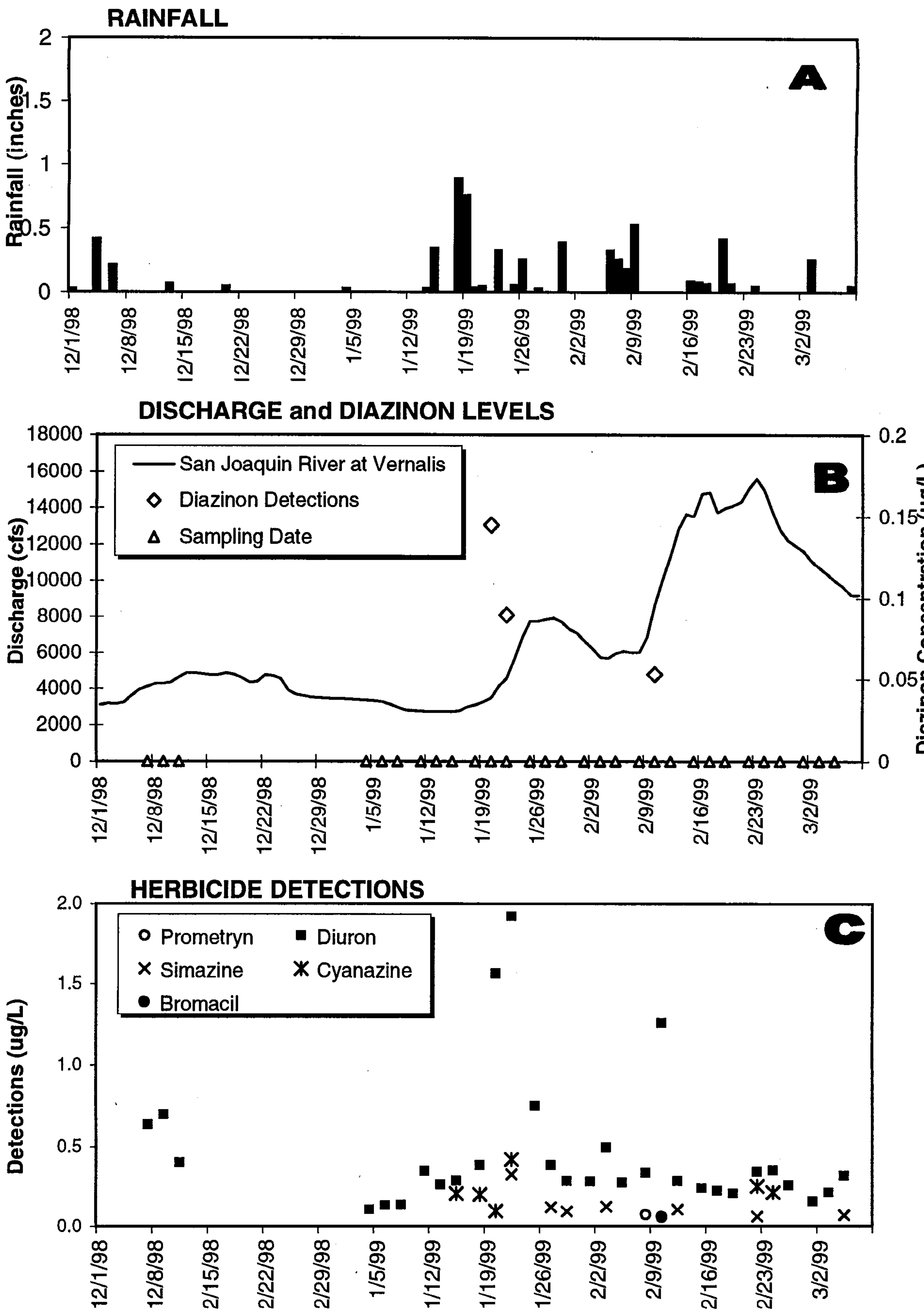

Figure 5. (A) Rainfall measured at Modesto; (B) discharge and diazinon concentrations measured in the San Joaquin River near Vernalis; (C) detections of herbicides, winter 1998-99 .

Table 1. California Department of Food and Agriculture, Center for Analytical Chemistry organophosphate and carbamate insecticide and herbicide screens for the San Joaquin River toxicity monitoring study.

Organophosphate Pesticides in Surface Water by GC Method: GC/FPD		**N-Methyl Carbamate in Surface Water by HPLC Method: HPLC/Post Column-fluorescence**		**Herbicides in Surface Water by HPLC Method: HPLC/UV detection and GC/Nitrogen Phosphorus detection (NPD)**	
Compound	**Reporting Limit (µg/L)**	**Compound**	**Reporting Limit (µg/L)**	**Compound**	**Reporting Limit (µg/L)**
Chlorpyrifos	0.04	Carbaryl	0.05	Atrazine	0.05
Diazinon[1]	0.04	Carbofuran	0.05	Bromacil	0.05
Dimethoate (Cygon)	0.05			Diuron	0.05
Fonofos	0.05			Cyanazine	0.2
Malathion	0.05			Hexazinone	0.2
Methidathion	0.05			Metribuzin	0.2
Methyl parathion	0.05			Prometon	0.05
Phosmet	0.05			Prometryn	0.05
				Simazine	0.05

[1] Diazinon was analyzed from a separate, unpreserved, split sample. Other OP and CB chemical samples were preserved with 3N HCl to a pH of 3-3.5 to retard analyte degradation. See text.

Table 2. Blind Spike Recoveries for the San Joaquin River and Sacramento River Studies.

Extraction Date	Study Number[a]	Sample Number	Screen	Pesticide	Spike Level	Recovery	Percent Recovery	Exceed CL[b]
1/19/99	178	169	OP	Fonofos	0.2	0.173	86.5	
				Phosmet	0.5	0.500	100	
1/19/99	178	170	CB	Carbaryl	0.1	0.105	105	UCL
				Carbofuran	0.2	0.188	94.0	
1/19/99	178	171	DI	Diazinon	0.1	0.088	88.0	
1/19/99	179	169	OP	Dimethoate	0.2	0.194	97.0	
				Methidathion	0.1	0.105	105	
1/19/99	178	172	TR	Hexazinone	0.5	0.528	106	
				Prometryn	0.3	0.306	102	
1/21/99	179	170	DI	Diazinon	0.2	0.188	94.0	
1/22/99	179	171	TR	Simazine	0.5	0.503	101	
				Bromacil	0.2	0.248	124	UCL
1/26/99	179	172	OP	Chlorpyrifos	0.2	0.186	93.0	
				Methyl Parathion	0.2	0.191	95.5	
1/28/99	179	174	TR	Prometryn	0.5	0.505	101	
				Atrazine	0.2	0.198	99.0	
1/29/99	179	173	DI	Diazinon	0.3	0.268	89.3	
2/2/99	178	233	OP	Dimethoate	0.2	0.206	103	
				Malathion	0.2	0.199	99.5	
2/2/99	178	234	CB	Carbaryl	0.2	0.182	91.0	
				Carbofuran	0.2	0.203	102	UCL
2/4/99	179	283	OP	Chlorpyrifos	0.2	0.179	89.5	
				Methidathion	0.3	0.290	96.7	
2/9/99	178	253	DI	Diazinon	0.1	0.100	100	
2/11/99	178	235	OP	Chlorpyrifos	0.2	0.125	62.5	LCL
				Fonofos	0.3	0.206	68.7	LCL
2/11/99	178	236	CB	Carbaryl	0.2	0.178	89.0	
				Carbofuran	0.2	0.175	87.5	
2/16/99	178	254	TR	Diuron	0.2	0.213	107	
				Metribuzine	0.5	0.525	105	UCL
2/22/99	179	285	TR	Cyanazine	0.5	0.420	84.0	
				Bromacil	0.2	0.167	83.5	LCL
2/22/99	178	240	TR	Prometon	0.3	0.260	86.7	
				Simazine	0.5	0.415	83.0	
2/23/99	178	238	CB	Carbaryl	0.3	0.289	96.3	
2/23/99	178	239	DI	Diazinon	0.15	0.139	92.7	
2/23/99	178	237	OP	Methyl Parathion	0.3	0.274	91.3	
				Phosmet	0.2	0.209	105	
2/23/99	179	284	DI	Diazinon	0.2	0.171	85.5	
2/25/99	178	242	CB	Carbofuran	0.3	0.235	78.3	
2/25/99	178	244	TR	Simazine	0.5	0.427	85.4	
2/25/99	178	241	OP	Methidathion	0.2	0.212	106	
2/26/99	178	243	DI	Diazinon	0.2	0.165	82.5	
3/1/99	179	340	TR	Bromacil	0.2	0.172	86.0	LCL
3/2/99	179	337	OP	Chlorpyrifos	0.2	0.191	95.5	
3/2/99	178	486	TR	Diuron	0.3	0.250	83.3	
3/2/99	178	483	OP	Chlorpyrifos	0.3	0.228	76.0	
3/2/99	178	485	DI	Diazinon	0.15	0.128	85.3	
3/2/99	179	339	DI	Diazinon	0.3	0.292	97.3	
3/2/99	179	338	CB	Carbofuran	0.2	0.157	78.5	LCL
3/2/99	178	484	CB	Carbaryl	0.2	0.186	93.0	
3/4/99	179	341	OP	Dimethoate	0.2	0.196	98.0	
3/4/99	179	342	TR	Cyanazine	0.5	0.483	96.6	
3/8/99	178	487	OP	Dimethoate	0.3	0.307	102.3	

[a] 178 refers to the study number for the Sacramento River, 179 refers to the SJR.

[b] CL=Control Limit; Upper CL (UCL), Lower CL (LCL). CLs for these pestcides are listed in Tables 3 through 6.

Table 3. Continuing Quality Control- Organophosphate Screen

Extraction Date	Sample Numbers	Percent Recovery							
		Chlorpyrifos	Diazinon	Dimethoate	Fonofos	Malathion	Methidathion	Methyl Parathion	Phosmet
12/11/98	178-1,7,19,25,31;179-1,7,13,9	83.8	80.0	98.0	66.0*	96.0	91.0	89.0	93.0
12/14/98	178-37;179-25	105	103	111	95.0	105	104	110	112
1/5/99	178-43,50,57;179-31,38	90.0	86.3	107	82.0	94.0	102	93.0	108
1/7/99	178-63,70,76;179-45,52	85.0	88.8	91.0	88.0	87.0	88.0	92.0	89.0
1/11/99	178-83,90;179-59	96.3	96.3	94.0	94.0	98.0	99.0	97.0	98.6
1/12/99	178-94,101,107;179-66,73	98.8	98.8	97.0	93.0	99.0	101	98.0	103
1/14/99	178-113,120,126;179-80,87	92.5	87.5	89.0	82.0	92.0	91.0	90.0	95.2
1/19/99	178-133,140,146, 152,169; 179-94,100,106	77.5	72.5	72.0	69.0	80.0	82.0	77.0	82.4
1/21/99	178-158,164,174;179-94,100,106	103	104	93.0	100	105	107	102	97.4
1/26/99	178-180,186,192,198; 179-142,130, 136,142,172	90.0	88.8	97.0	82.0	92.0	91.0	90.0	90.2
1/28/99	178-136,143,149, 155;179-97,103,109	98.8	91.3	97.0	88.0	97.0	93.0	95.0	85.4
1/28/99	178-204,210,214, 220;179-148,154	104	98.8	99.0	97.0	105	101	101	94.4
2/2/99	178-226,232,233, 260,266;179-160,175,181	88.8	83.8	86.0	83.0	90.0	90.0	88.0	87.0
2/2/99	178-161,167,177	83.8	82.5	87.0	74.0	89.0	91.0	84.0	92.0
2/9/99	178-290,296,302, 306,312;179-200,206,212	82.5	80.0	88.0	73.0	86.0	88.0	84.0	88.4
2/4/99	178-272,278,284; 179-166,190,196,283	86.3	83.8	86.0	74.0	92.0	91.0	87.0	89.8
2/11/99	178-235,318,324, 328,334;179-218,224	93.8	91.3	96.0	83.0	79.0	96.0	95.0	97.0
2/16/99	178-340,346,352, 358;179-230,236,242	85.0	81.3	91.0	77.0	89.0	90.0	85.0	91.0
2/18/99	178-364,370,376; 179-249,254	92.5	88.8	92.0	87.0	95.0	96.0	92.0	96.0
2/23/99	178-237,382,388, 394,398,404;179-260,266,270,276	93.8	93.8	92.0	93.0	94.0	94.0	92.0	93.8
2/25/99	178-241,410,416, 422;179-282,294,300	88.8	87.5	86.0	81.0	93.0	88.0	89.0	92.6
3/2/99	178-428,434,438, 444,450,483;179-304,310,316,337	97.5	96.3	87.0	94.0	99.0	100	97.0	97.2
3/4/99	178-456,462,468;179-322,325,341,346	95.0	93.8	99.0	93.0	98.0	103	97.0	92.6
3/8/99	178-474,480,487; 179-329	95.0	91.3	94.0	95.0	98.0	97.0	96.0	91.4
Average Recovery		91.9	89.5	92.9	86.0	93.8	94.8	92.5	94.0
Standard Deviation		7.16	7.67	7.76	8.74	6.88	6.28	6.96	6.66
CV		7.79	8.57	8.36	10.17	7.33	6.63	7.52	7.08
Upper Control Limit		112	109	120	111	113	120	118	120
Upper Warning Limit		106	103	113	103	107	113	111	113
Lower Warning Limit		81.8	77.6	85.6	73.6	82.3	83.8	82.7	84.5
Lower Control Limit		75.7	71.4	78.8	66.3	76.1	76.6	75.7	77.4

*Highlighted cells are percent recoveries exceeding control limits

Table 4. Continuing Quality Control-Carbamate Screen

Extraction Date	Sample Numbers	Percent Recovery	
		Carbofuran	Carbaryl
12/8/98	178-2,8,14;179-2,8	88.8	94.0
12/10/98	178-20,26,32; 179-14,20	89.4	98.2
12/14/98	178-38;179-26	97.0	97.0
1/6/99	178-44,51,58;179-32,39	90.4	95.0
1/7/99	178-64,71,77;179-46,53	87.9	98.1
1/12/99	178-84,91,95, 102,108;179-60,67,74	92.7	101*
1/14/99	178-114,121,127;179-81,88	90.1	98.0
1/19/99	178-134,141, 147,153,170; 179-95,101,107	98.1	93.6
1/21/99	178-175,165,159;179-119,113	102	103
1/26/99	178-182,187,195, 199;179-125,131,143	104	106
1/28/99	178-205,211, 215,221;179-149,155	101	96.8
2/2/99	178-227,234,255, 261,267;179-161,176,182	91.7	97.1
2/4/99	178-273,279,285;179-167,191,197	90.4	96.2
2/9/99	178-291,297,303, 307,313;179-201,207,213	90.2	102
2/11/99	178-236,319,325, 329,335;179-219,225	88.4	89.6
2/16/99	178-341,347,353, 359;179-231,237,243	96.2	99.4
2/18/99	178-365,371,377;179-249,255	92.1	99.4
2/23/99	178-238,383,389, 395,399,405;179-261,267,271,277	101	99.5
2/25/99	178-242,411,417, 423;179-289,295,299	85.7	99.3
3/2/99	178-429,435,439, 445,451,484;179-305,311,317,338	93.0	98.9
3/4/99	178-457,463,469;179-323,326,347	92.1	101
3/8/99	178-475,481;179-330	83.2	97.6
Average Recovery		93.0	98.1
Standard Deviation		5.5	3.5
CV		5.9	3.6
Upper Control Limit		99.8	99.5
Upper Warning Limit		95.7	96.0
Lower Warning Limit		79.2	82.2
Lower Control Limit		75.0	78.2

*Highlighted cells are percent recoveries exceeding control limits

Table 5. Continuing Quality Control-Diazinon Analysis

Extraction Date	Sample Numbers	Percent Recovery
		Diazinon
12/9/98	178-3,9,15;179-3,9	97.5
12/10/98	178-21,27,33;179-15,21	78.8
12/14/98	178-39;179-27	91.3
1/7/99	178-45,52,59, 65,72,78;179-33,40,47,54	87.5
1/11/99	178-85,92;179-61	92.5
1/12/99	178-96,103,109;179-68,75	93.8
1/14/99	178-115,122,128;179-82,89	87.5
1/19/99	178-135,148,154, 171;179-82,89	78.8
1/21/99	178-160,166,176;179-114,120,170	102.5
1/22/99	179-122	101.3
1/26/99	178-181,184,188, 194,200;179-126,132,138,144	88.8
1/29/99	178-206,212,216, 222;179-150,156,173	90.0
2/2/99	178-162,168,178	88.8
2/3/99	178-228,256,262, 268:179-162,177,183	96.3
2/4/99	178-274,280,286;179-168,192,198	92.5
2/9/99	178-253,292,298, 304,308,314;179-202,208,214	91.3
2/11/99	178-320,326,330, 336;179-220,226	92.5
2/16/99	178-342,348,354, 360;179-232,238,244	88.8
2/18/99	178-366,372,378;179-250,256	88.8
2/23/99	178-239,384,396,400, 406;179-262,268, 272,278,284	95.0
2/26/99	178-243,412,418, 424;179-290,296,298	93.8
3/2/99	178-430,436,440, 446,452,485;179-306,312,318,339	88.8
3/4/99	178-458,464,470;179-324,327,348	95.0
3/8/99	178-476,482;179-331	95.0
Average Recovery		91.5
Standard Deviation		5.6
CV		6.1
Upper Control Limit		109
Upper Warning Limit		103
Lower Warning Limit		77.6
Lower Control Limit		71.4

Table 6. Continuing Quality Control- Triazine/Diuron/Bromacil Screen

Extraction Date	Sample Numbers	Percent Recovery								
		Atrazine	Bromacil	Diuron	Cyanazine	Hexazinone	Metribuzin	Prometon	Prometryn	Simazine
1/5/99	178-48,55,62;179-35,43	94.0	115*	107	101	105	88.6	98.8	94.6	91.6
1/5/99	178-48,55,62;179-35,43	100	111	97.0	97.0	110	90.0	87.0	76.0	95.0
1/8/99	178-68,75,81;179-35,43	100	112	118	98.8	109	103	86.0	71.0	82.6
1/8/99	178-68,75,81;179-50,57	99.0	103	113.6	96.4	114	100	87.4	84.6	91.8
1/11/99	178-88,93;179-64	80.0	120	92.0	80.3	103	87.0	111	108	108
1/11/99	178-88,93;179-64	78.8	92.6	95.0	84.4	105	90.4	82.6	90.6	82.4
1/13/99	178-99,106,112;179-71,78	97.0	99.0	105	95.0	111	90.3	93.0	104	107
1/14/99	178-118,125,131;179-85,91	82.0	88.0	99.0	83.5	115	88.0	91.0	99.0	88.0
1/15/99	178-4,10,16,24,36,42;179-6,12,18,24,30	95.0	110	103	99.8	110	102	89.0	91.0	96.0
1/19/99	178-138,145,151,157,172;179-99,105,111	114	93.0	103	86.0	109	86.5	107	112	87.0
1/22/99	178-163,173,179;179-123,171	102	117	100	97.3	112	90.0	99.7	106	107
1/25/99	178-185; 179-129,135	100	121	89.0	105	104	94.8	98.0	100	105
1/28/99	178-209,213,219,225;179-159,174	96.0	117	103	102	103	93.5	101	110	96.0
1/26/99	178-191,203;179-141,147	92.0	99.0	106	96.0	100	87.5	95.0	103	95.0
1/29/99	178-231;179-165	91.0	102	94.0	92.3	94.8	89.3	88.0	108	93.0
2/2/99	178-259,265,271;179-180,186	100	103	80.0	105	96	86.8	112	109	109
2/4/99	178-277,283,289;179-189,195,199	86.0	107	76.0	87.8	94.8	77.0	89.0	87.0	110
2/16/99	178-254,295,301,305,311,317,323,327,333, 339	95.0	87.0	104	94.3	97.5	91.5	113	103	103
2/17/99	179-205,211,217,223,229	94.0	90.0	98.0	94.3	99.8	89.3	84.0	82.0	98.0
2/17/99	178-345,351,357, 363;179-235,241,247	89.0	98.0	97.0	96.5	105	89.5	78.0	79.0	93.0
2/18/99	178-369,375,381;179-253,259	106	111	105	97.8	99.0	91.5	100	95.0	109
2/22/99	178-240,387;179-265,269,285	103	103	93.0	95.3	95.3	91.5	105	118	119
2/22/99	178-393,397,403,409;179-275,281	103	104	108	92.8	96.5	87.3	98.0	88.0	101
2/25/99	178-244,415,421,427;179-293,297,303	94.0	97.0	99.0	92.3	92.0	85.0	87.0	88.0	94.0
3/1/99	178-433,437;179-309,340	93.0	105	106	99.5	101	96.8	109	109	112
3/2/99	178-443,449,455,486;179-315,321	94.0	119	123	87.3	99.8	92.0	111	109	118
3/4/99	178-461,467,473;179-328,342,345,351	91.0	97.0	115	92.5	102	94.3	80.0	81.0	102
Average Recovery		95.1	104	101	94.4	103	90.8	95.6	96.5	100
Standard Deviation		7.85	10.0	10.4	6.34	6.44	5.29	10.5	12.6	9.95
CV		8.25	9.61	10.3	6.71	6.25	5.82	11.0	13.1	9.98
Upper Control Limit		121	109	117	121	123	105	109	115	126
Upper Warning Limit		114	103	108	114	115	101	103	108	118
Lower Warning Limit		85.0	92.1	74.6	87.4	84.5	84.5	92.1	79.1	86.4
Lower Control Limit		77.7	86.5	66.2	80.7	76.8	80.4	86.5	71.9	78.5

*Highlighted cells are percent recoveries exceeding control limits

Table 7. Concentrations of pesticides (ppb) detected in samples from Orestimba Creek and the San Joaquin River, winter 1998-99.

ORESTIMBA CREEK at RIVER ROAD								SAN JOAQUIN RIVER near VERNALIS							
Sampling Date	Diazinon	Bromacil	Cyanazine	Diuron	Prometryn	Simazine	Acute Toxicity (percent survival[1])	Diazinon	Bromacil	Cyanazine	Diuron	Prometryn	Simazine	Chronic Toxicity (percent survival[1])	Chronic Toxicity (offspring per female[1])
12/7/98	*nd*[2]	*nd*	*nd*	0.176	*nd*	*nd*	75/100	*nd*	*nd*	*nd*	0.633	*nd*	*nd*		
12/9/98	*nd*	*nd*	*nd*	0.201	*nd*	*nd*	100/95	*nd*	*nd*	*nd*	0.695	*nd*	*nd*		
12/11/98								*nd*	*nd*	*nd*	0.400	*nd*	*nd*	100/100	31.1/23.6
1/4/99	*nd*	*nd*	*nd*	0.288	*nd*	*nd*	95/100	*nd*	*nd*	*nd*	0.103	*nd*	*nd*		
1/6/99	*nd*	*nd*	*nd*	0.331	*nd*	*nd*	100/100	*nd*	*nd*	*nd*	0.131	*nd*	*nd*		
1/8/99								*nd*	*nd*	*nd*	0.134	*nd*	*nd*	80/90[3]	19.1/18.4
1/11/99	*nd*	*nd*	*nd*	0.277	*nd*	*nd*	100/90	*nd*	*nd*	*nd*	0.345	*nd*	*nd*		
1/13/99	*nd*	*nd*	*nd*	1.66	*nd*	*nd*	100/100	*nd*	*nd*	*nd*	0.262	*nd*	*nd*		
1/15/99								*nd*	*nd*	0.206	0.288	*nd*	*nd*	100/90	37.1/22.3
1/18/99	*nd*	*nd*	*nd*	0.778	*nd*	*nd*	100/100	*nd*	*nd*	0.199	0.383	*nd*	*nd*		
1/20/99	*nd*	*nd*	*nd*	0.759	*nd*	*nd*	100/90	0.145	*nd*	0.0970	1.56	*nd*	*nd*		
1/22/99								0.0900	*nd*	0.419	1.92	*nd*	0.324	80/100	24.0/20.8
1/25/99	*nd*	*nd*	*nd*	0.783	*nd*	*nd*	100/90	*nd*	*nd*	*nd*	0.747	*nd*	*nd*		
1/27/99	*nd*	*nd*	*nd*	0.567	*nd*	0.102	100/95	*nd*	*nd*	*nd*	0.383	*nd*	0.118		
1/29/99								*nd*	*nd*	*nd*	0.285	*nd*	0.0920	80/100	26.4/20.8
2/1/99	*nd*	0.0840		0.922	*nd*	*nd*	100/90	*nd*	*nd*	*nd*	0.281	*nd*	*nd*		
2/3/99	*nd*	*nd*	*nd*	0.607	*nd*	*nd*	100/100	*nd*	*nd*	*nd*	0.492	*nd*	0.123		
2/5/99								*nd*	*nd*	*nd*	0.276	*nd*	*nd*	100/100	26.3/24.8
2/8/99	*nd*	*nd*	*nd*	0.466	*nd*	*nd*	95/95	*nd*	*nd*	*nd*	0.334	0.0705	*nd*		
2/10/99	*nd*	*nd*	*nd*	0.0992	*nd*	*nd*	100/100	0.0530	0.0588	*nd*	1.26	0.0530	*nd*		
2/12/99								*nd*	*nd*	*nd*	0.285	*nd*	0.103	100/100	32.4/24.6
2/15/99	*nd*	*nd*	*nd*	0.0610	*nd*	*nd*	100/100	*nd*	*nd*	*nd*	0.238	*nd*	*nd*		
2/17/99	*nd*	*nd*	*nd*	0.0750	*nd*	*nd*	100/100	*nd*	*nd*	*nd*	0.223	*nd*	*nd*		
2/19/99								*nd*	*nd*	*nd*	0.207	*nd*	*nd*	100/100	31.8/25.2
2/22/99	*nd*	0.0796	0.369	0.741	0.076	0.0930	100/95	*nd*	*nd*	0.252	0.339	*nd*	0.0590		
2/24/99	*nd*	*nd*	*nd*	0.358	*nd*	*nd*	100/100	*nd*	*nd*	0.213	0.349	*nd*	*nd*		
2/26/99								*nd*	*nd*	*nd*	0.258	*nd*	*nd*	100/90	29.2/22.6
3/1/99	*nd*	*nd*	*nd*	0.221	*nd*	0.0660	100/100	*nd*	*nd*	*nd*	0.156	*nd*	*nd*		
3/3/99	*nd*	0.0886	*nd*	0.233	*nd*	0.0760	100/90	*nd*	*nd*	*nd*	0.211	*nd*	*nd*		
3/5/99								*nd*	*nd*	*nd*	0.317	*nd*	0.0700	100/100	23.4/18.4

1) Two numbers are reported for all toxicity tests. The first number is the result from the sample and the second is the result from the corresponding control. 2) nd=none detected

3) Test re-started at 77 hours due to failed control.

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